COUPLED ^{190}Pt-^{186}Os AND ^{187}Re-^{187}Os ISOTOPIC SYSTEMS: DETECTION OF POSSIBLE CORE-MANTLE INTERACTION AND ESTIMATION OF SULFUR IN THE OUTER CORE. J.W.Morgan, R.J.Walker, M.I. Smoliar, Department of Geology, University of Maryland, College Park MD 20742; E. S. Beary, NIST, Gaithersburg MD 20899 and P.A. Baedecker, USGS Reston VA 22092.

We have developed a simple technique for the simultaneous application of the ^{187}Re-^{187}Os and ^{190}Pt-^{186}Os isotope systems to geochemical problems. The coupled systems are attractive to both basic research and economic geology since they link three highly siderophile elements, two of which are platinum group elements (PGE). For this initial work we have studied the ^{190}Pt-^{186}Os systematics of two groups of samples for which we already have extensive ^{187}Re-^{187}Os data; the IIAB iron meteorites, and a suite of Noril'sk ores that are related to the plume-derived Siberian flood basalts (SFB) **[1,2]**.

Exploitation of the ^{190}Pt-^{186}Os system has been deterred by two factors; the long half life of ^{190}Pt as determined by thick source α counting **[3]**; and the extremely low abundance of ~0.0124% for the *p*-process isotope ^{190}Pt **[4]**. Multicollector NTIMS now enables the detection of ^{186}Os/^{188}Os enrichment even in materials with modest ^{190}Pt/^{188}Os.

Experimental Methods*:** Using ^{198}Pt as spike, the Pt chemistry was grafted on to existing separations for Re and Os. The procedure for alkaline fusion or Carius tube digestion follows that standard for Re and Os. Osmium is distilled from $\geq 5N$ H_2SO_4 , and Re and Pt are recovered by anion exchange. Re is eluted with 4 *N* HNO_3 and the column washed with 0.8 *N* HNO_3. Platinum (and Pd) may be quantitatively eluted with a few mL of 0.1 *M* thiourea-0.1 *M* HCl. Thiourea is destroyed by ***cautious addition of conc. HNO_3 in a covered beaker. The resulting NH_4NO_3 can be removed by digestion with *aqua regia*. The solution contains a little H_2SO_4 from oxidation of the thiourea. Immediately before ICP-MS analysis, a solution in ~5% HNO_3 is prepared containing ~10ng/mL^{-1} of the most abundant Pt isotope. ^{195}Pt/^{198}Pt is measured using a *VG PQ2* ICP source mass spectrometer with a concentric nebulizer and a spray chamber water-cooled to 2° C. The 2σ internal reproducibility is generally 0.3 to 0.5%. Replicate dissolutions of the IIAB iron meteorite Filomena gave 25.3 , 25.1 and 25.2 ppm respectively, suggesting a 2σ external reproducibility of ~0.8%. Blanks averaged 1.1 ng and the correction was negligible for most samples. Osmium isotopic measurements were made with a *Sector54* multicollector solid source mass spectrometer using Pt filaments. For most purposes, ratios were measured in the static mode. For highest precision, the dynamic mode was used.

Results and Discussion: A suite of 11 Ni-PGE ores from Noril'sk-Talnakh, Siberia was analysed for Pt and Os by alkaline fusion, and 6 of these were replicated by Carius tube digestion. Osmium replicates agree well, generally within the error of the isotopic determination. Pt replicates are more variable in a few low Pt ores, but correlate with variation of ^{186}Os/^{188}Os where these are significant. A ^{186}Os/^{188}Os *versus* ^{190}Pt/^{188}Os isochron has a slope of $(3.874 \pm 0.043) \times 10^{-4}$ (Fig. 1). The Noril'sk ores are derived from, and presumably contemporaneous with, the voluminous SFB, which have been precisely dated at 251.2 ± 0.3 Ma **[5]**. The Noril'sk isochron, therefore, implies a ^{190}Pt decay constant, λ_{Pt}, of $(1.542 \pm 0.023) \times 10^{-11}$a^{-1} and a half life of 450 ± 7 Ga. This half life is considerably shorter than the mean α-counting value, but is within the 2σ error of 2 of the 4 compiled results **[3]**.

We verified the new half life value by analyzing a suite of 11 IIAB iron meteorites with a measured Re-Os isochron age of 4537 ± 8 Ma **[1]** (Fig. 2). For the 14 data (including replicates for Filomena and Navajo), the Pt-Os isochron age of 4500 ± 100 Ma suggests that the new ^{190}Pt half life is accurate within the stated errors.

The SFB are thought to be derived from a large plume possibly originating at the core-mantle boundary (CMB). Like many rocks of presumed plume origin, SFB and the associated Noril'sk ores have radiogenic ^{187}Os/^{188}Os, which in the ores average +7% relative to contemporary upper mantle **[2]**. Repeated measurements were made in the dynamic mode of unspiked samples of two Os-rich materials with low ^{190}Pt/^{188}Os (Fig 3). Noril'sk bore hole sample KZ 1713- 931.1 has 550 ppb Os and ^{190}Pt/^{188}Os = 0.00137, a slightly subchondritic value compared to the ratio we measured in eight E chondrites (average ^{190}Pt/^{188}Os = 0.00166). As an upper mantle surrogate, an osmiridium was chosen whose ^{187}Os/^{188}Os = 0.12427, a value very similar to that of modern abyssal peridotites where ^{187}Os/^{188}Os = 0.1246. ^{186}Os/^{188}Os averages 0.119849 ± 4 and 0.119834 ± 2 in Noril'sk ore and osmiridium, respectively, corresponding to an enrichment of 0.125 ± 0.037 per mil in the SBF relative to the upper mantle.

During the early stages of crystallization of asteroidal metallic cores as represented by magmatic iron meteorite groups, Re/Os and Pt/Os is consistently enriched relative to chondritic in the melt. The Earth's core is 5.5% crystallized, and ^{187}Re/^{188}Os and ^{190}Pt/^{188}Os in the liquid outer core may consequently be significantly enriched over the initial chondritic value. Geophysical evidence suggests that the D″ layer near

the CMB may be infiltrated by outer core liquid. Walker *et al.* **[6]** showed that suprachondritic $^{187}Os/^{188}Os$ and $^{186}Os/^{188}Os$ in plume sources could be explained by siderophile contamination of the plume source from the outer core and predicted that $^{186}Os/^{188}Os$ should be enriched by ~ 0.1 per mil. The new data confirm this prediction and enable the analysis to go a step further.

In IIA iron meteorites, the slopes of log Re and log Pt *vs.* log Os enable us to relate k_{Re} and k_{Pt} in terms of one variable, the Os partition coefficient k_{Os}. If the relative partitioning behavior of the 3 elements is similar in asteroidal and terrestrial cores, $^{190}Pt/^{188}Os$ and $^{187}Re/^{188}Os$ in the Earth's outer core are defined solely by k_{Os}. For the simplest model where the inner core formed early, enrichments of $^{186}Os/^{188}Os = 0.125 \pm 0.037$ per mil and $^{187}Os/^{188}Os = 7.1 \pm 0.9$ percent in the SBF plume both correspond to $k_{Os} = 17.5 \pm 2.5$ (Fig 4). For a core with 0.6% P, experimental partitioning data **[7]** suggests that the outer core may contain 14.5 ± 2.2 % S. This S value is at the upper end of most estimates but may be possible for an overall terrestrial composition similar to enstatite chondrites. We recognize, however, that at core pressures solid Fe is likely to be ε (hcp) Fe rather than γ (fcc) Fe. This phase change may enhance *k* for such hcp metals as Re and Os, but perhaps not for fcc Pt unless there is a corresponding high pressure form.

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REFERENCES: [1] Smoliar *et al.*1996, *Science* **271,** 1099. **[2]** Walker *et al.* 1994, *GCA* **58,** 4179. **[3]** Al-Bataina & Jänecke 1987, *Radiochim. Acta* **42,** 159. **[4]** Walker *et al.*1991, *EPSL* **105**, 416. **[5]** Kamo *et al.* 1996, *GCA* **60**, 3505. **[6]** Walker *et al.* 1995, *Science* **269,** 819**. [7]** Jones & Jurewicz 1994, *EOS* **75,** 694.

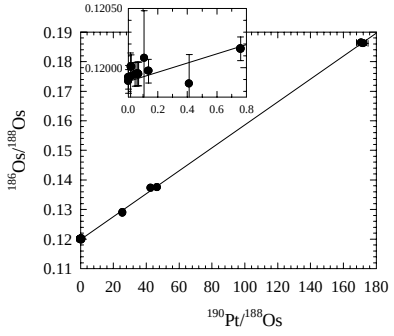

Figure 1. $^{190}Pt/^{188}Os$ versus $^{186}Os/^{188}Os$ for Noril'sk, Siberia ore samples. Inset shows expanded scale view of data for samples with low Pt/Os.

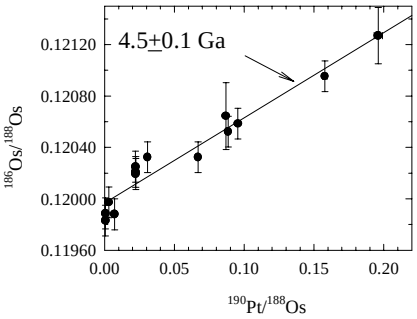

Figure 2 . $^{190}Pt/^{188}Os$ versus $^{186}Os/^{188}Os$ for group IIAB iron meteorites. Best fit isochron defines an age of 4.5+1 Ga using the ^{190}Pt decay constant obtained from the Noril'sk isochron.

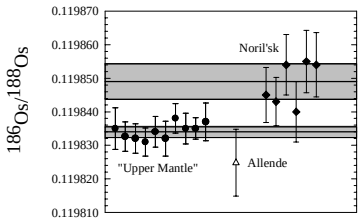

Figure 3. $^{186}Os/^{188}Os$ measurements for a modern upper mantle osmiridium, the carbonaceous chondrite Allende, and Noril'sk ore 1713-931. Shaded bands represent the 2σ sdm uncertainties for repeated measurements of the osmiridium and the ore.

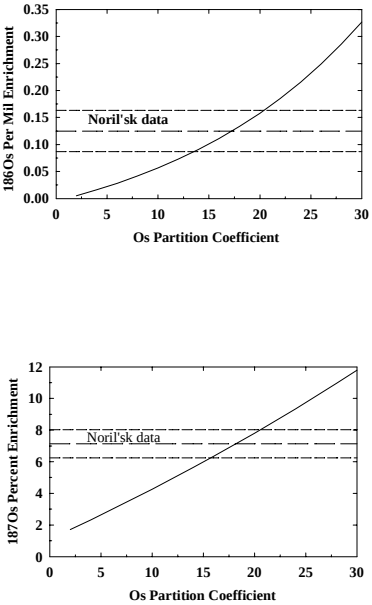

Figure 4. Predicted enrichments in ^{186}Os (upper) and ^{187}Os (lower) for the outer core relative to k_{Os} assuming early inner core formation. In both isotope systems intersection with Noril'sk data gives similar values of $k_{Os} = 17.5 \pm 2.5$..